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GEOLOGY

Oxygen isotopic evidence for accretion of Earth's water before a high-energy Moon-forming giant impact

Richard C. Greenwood,^{1*} Jean-Alix Barrat,² Martin F. Miller,^{1,3} Mahesh Anand,^{1,4} Nicolas Dauphas,⁵ Ian A. Franchi,¹ Patrick Sillard,⁶ Natalie A. Starkey¹

The Earth-Moon system likely formed as a result of a collision between two large planetary objects. Debate about their relative masses, the impact energy involved, and the extent of isotopic homogenization continues. We present the results of a high-precision oxygen isotope study of an extensive suite of lunar and terrestrial samples. We demonstrate that lunar rocks and terrestrial basalts show a 3 to 4 ppm (parts per million), statistically resolvable, difference in $\Delta^{17}\text{O}$. Taking aubrite meteorites as a candidate impactor material, we show that the giant impact scenario involved nearly complete mixing between the target and impactor. Alternatively, the degree of similarity between the $\Delta^{17}\text{O}$ values of the impactor and the proto-Earth must have been significantly closer than that between Earth and aubrites. If the Earth-Moon system evolved from an initially highly vaporized and isotopically homogenized state, as indicated by recent dynamical models, then the terrestrial basalt-lunar oxygen isotope difference detected by our study may be a reflection of post-giant impact additions to Earth. On the basis of this assumption, our data indicate that post-giant impact additions to Earth could have contributed between 5 and 30% of Earth's water, depending on global water estimates. Consequently, our data indicate that the bulk of Earth's water was accreted before the giant impact and not later, as often proposed.

INTRODUCTION

The now classic formulation of the Moon-forming giant impact hypothesis envisaged an oblique impact between the proto-Earth and a Mars-sized body (1). Numerical simulations based on this model indicated that the Moon accreted from a debris disc containing approximately 70% impactor-derived material (1). If the impactor had a different oxygen isotopic composition ($\Delta^{17}\text{O}$) to the proto-Earth, a prediction of this model is that Earth and the Moon should display resolvable isotopic differences (see Results for the definition of $\Delta^{17}\text{O}$) (2, 3). However, with a sole exception (4), high-precision studies have failed to detect a difference between Earth and the Moon (5–8). To explain this apparent discrepancy, it has been proposed that isotopic equilibration took place within a post-impact, melt-vapor disc (9). Studies of silicon (10) and titanium (11) isotopic variation have also revealed no differences between Earth and the Moon. In addition, tungsten isotope studies indicate that Earth and the Moon initially had a similar ^{182}W composition (12). The fact that both tungsten and titanium show no isotopic differences between Earth and the Moon is potentially significant because both are very refractory elements and, thus, unlikely to have been significantly affected by the proposed post-impact equilibration (9).

The isotopic similarity between Earth and the Moon, combined with a reassessment of the angular momentum constraints, has led to the formulation of high-energy models, which invoke nearly complete mixing between the impactor and the target (2, 3). Recent modeling studies suggest that typical rocky planets may be vaporized multiple times by giant impacts (13, 14). This process results in the formation of an extended structure termed a “synestia,” initially composed principally

of silicate vapor and comprising a co-rotating inner region connected to a disc-like outer region. When applied to the formation of the Earth-Moon system, the synestia model suggests that the Moon formed from condensing liquid beyond the Roche limit, with the bulk of the structure contracting to form Earth (13). Such a structure would involve complete isotopic equilibration for the bulk of the Earth-Moon system (13), with the possibility that restricted regions of Earth's deep mantle might still retain some evidence of pre-giant impact isotopic signatures (15). Potassium isotope analyses, which show a small resolvable Earth-Moon difference, have been interpreted as being consistent with results of high-energy impact simulations (16).

However, complete isotopic re-equilibration in the wake of the giant impact has been questioned by a study that detected a 12 ± 3 ppm (parts per million) (SEM) Earth-Moon $\Delta^{17}\text{O}$ difference (4). Subsequently, this finding was challenged by a study that was unable to detect this isotopic difference at a level of ± 5 ppm (SEM) (5). Lack of significant isotopic differences between Earth and the Moon has also been explained by a terrestrial accretion model, based on the contrasting affinities of a range of elements (O, Ca, Ti, Cr, Ni, Mo, and Ru), which predicts that both the impactor and the proto-Earth formed from the same enstatite chondrite-like precursor materials, making large Earth-Moon isotopic differences unlikely (17).

RESULTS

Here, we present the results of a detailed, high-precision oxygen isotope investigation, based on a more extensive suite of both lunar and terrestrial samples than in any previous study. Oxygen isotopic data are reported using the δ notation: $\delta^i\text{O} = [(^{i}\text{O}/^{16}\text{O})_{\text{sample}}/(^{i}\text{O}/^{16}\text{O})_{\text{VSMOW}}] - 1$, where $i = 17$ or 18 and VSMOW is the Vienna Standard Mean Ocean Water reference material. Results are, by convention, reported as per mil (‰). $\Delta^{17}\text{O}$, which represents the deviation from an assigned reference fractionation line, has been calculated according to (18) $\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda \ln(1 + \delta^{18}\text{O}) + \gamma$ and reported as parts per million. We chose to assign $\lambda = 0.5262$ and $\gamma = -64$ ppm (see Materials and Methods for further details).

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Lunar whole rock samples ($n = 17$) covering all the main lithological units, from all six Apollo landings, have been analyzed, as well as lunar mineral separates ($n = 14$) (see Materials and Methods) (table S1). Lunar rocks and mineral separates are compared to terrestrial mafic rocks, comprising basalts ($n = 20$) and a mantle xenolith (tables S1 and S3). In the terrestrial sample set, we also include our previously published olivine data (19). Data from previous studies (19, 20) have been recalibrated against VSMOW (see Materials and Methods).

The oxygen isotopic compositions of the lunar and terrestrial samples analyzed in this study, and other extraterrestrial materials that plot close to the terrestrial fractionation line (TFL), are shown in Fig. 1. Lunar whole rocks have relatively homogeneous oxygen isotope compositions, with $\delta^{18}\text{O}$ values that range from $5.64 \pm 0.02\text{‰}$ (2 SD) to $6.19 \pm 0.02\text{‰}$ (2 SD) and $\Delta^{17}\text{O}$ values from 2 to 20 ppm (Fig. 2 and table S1). In comparison, terrestrial whole rocks show a wider spread in $\delta^{18}\text{O}$, ranging from $5.03 \pm 0.12\text{‰}$ (2 SD) to $6.27 \pm 0.15\text{‰}$ (2 SD) and have $\Delta^{17}\text{O}$ values from -4 to 15 ppm (Fig. 2 and table S1). However, the mean $\delta^{18}\text{O}$ values of the lunar and terrestrial whole rocks are close, $5.92 \pm 0.28\text{‰}$ (2 SD) and $5.79 \pm 0.69\text{‰}$ (2 SD), respectively. Terrestrial and lunar samples show similar slopes and y -axis intercepts on plots of $10^3 \ln(1 + \delta^{17}\text{O})$ versus $10^3 \ln(1 + \delta^{18}\text{O})$ (figs. S1 to S3).

It is clear from Fig. 2 that lunar and terrestrial samples show a significant level of overlap with respect to $\Delta^{17}\text{O}$, whereas the aubrites (20) are fully resolved on this plot. There is a 3 ppm difference between the average $\Delta^{17}\text{O}$ value of lunar samples compared to that of terrestrial samples, with the full suite of lunar whole rocks and mineral separates ($n = 31$) having a mean $\Delta^{17}\text{O}$ composition of 10 ± 2 ppm (2 SEM), compared to 7 ± 2 ppm (2 SEM) for all terrestrial samples and mineral separates ($n = 37$) (Fig. 2 and table S1). When terrestrial basalts [$\Delta^{17}\text{O} = 6 \pm 2$ ppm (2 SEM) ($n = 20$)] are compared to lunar whole rocks, this difference increases to 4 ppm (Fig. 3).

To test the significance of the 3 ppm difference between the two data sets, we performed an unpaired t test (test 1) (table S2). This gave a P value of 0.032, which is below the 0.05 threshold and indicates that

this 3 ppm difference is statistically significant. Excluding samples with SEM values >6 ppm (test 2) (table S2) does not significantly alter this result. The results of a t test for terrestrial basalts and lunar whole rocks (test 3) returned a P value of 0.014, well below the 0.05 threshold (table S2). Although this P value increased when samples with SEM values >6 ppm were excluded, the results of both tests (tests 3 and 4) indicate that this 4 ppm difference between terrestrial basalts and lunar whole rocks is statistically significant (table S2). In comparison, all t tests on terrestrial olivine samples (tests 4 to 8) (table S2) indicate that the 1 to 2 ppm $\Delta^{17}\text{O}$ differences they show with lunar samples are not statistically significant, returning P values that are considerably above the 0.05 threshold.

To further scrutinize the statistical significance of our data, we used the bootstrap technique with 10^6 replications on both the averaged data (table S1) and raw data (see separate Excel file in other Supplementary Materials). The results of these analyses are given in the “Further statistical analysis” section (see the Supplementary Materials) and, in conformity with the t tests, indicate that the 3 to 4 ppm difference between the lunar and terrestrial data sets is statistically significant. Our results contrast with those of Young *et al.* (5), undertaken on a somewhat smaller data set than the present one, which concluded that lunar and terrestrial rocks are indistinguishable with respect to $\Delta^{17}\text{O}$ at a level of ± 5 ppm.

Our results indicate a dichotomy in terrestrial $\Delta^{17}\text{O}$ values, with no significant difference between lunar rocks and terrestrial olivine (both high- and low- $^3\text{He}/^4\text{He}$ varieties), but a statistically significant difference of 3 to 4 ppm when basaltic samples are included in the terrestrial data set. Contamination of the terrestrial basalts (mainly submarine quenched glasses) by seawater is an unlikely explanation for this effect. When compared to VSMOW, natural seawater samples have a $\Delta^{17}\text{O}$ composition of -5 ppm (21), which, relative to our reference line, would give seawater a $\Delta^{17}\text{O}$ value of $+59$ ppm (see Materials and Methods), and so any interaction between seawater and the terrestrial basalts would have the effect of increasing their $\Delta^{17}\text{O}$ values and thereby reducing the difference between them and the lunar rocks. It could be argued that some form of seawater

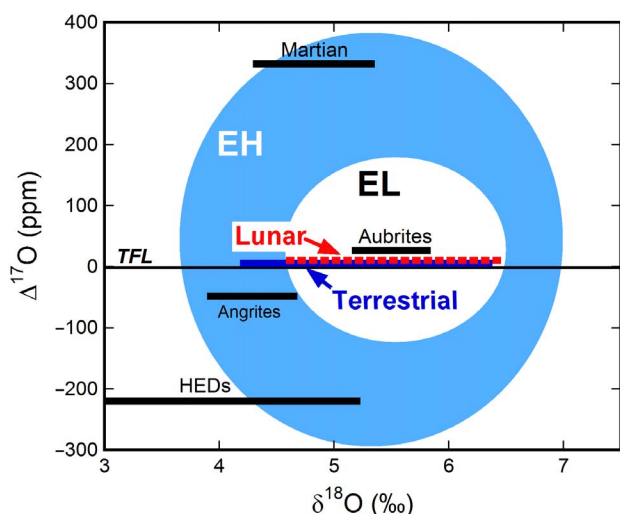


Fig. 1. Oxygen isotope composition of terrestrial and lunar samples shown in relation to various meteorite groups that plot close to the TFL. Enstatite chondrites (EH and EL groups) (26) are shown as circular filled and unfilled fields. Aubrites, HEDs (howardites, eucrites, diogenites), angrites, and Martian meteorites are shown as bars to represent the $\delta^{18}\text{O}$ range and mean average $\Delta^{17}\text{O}$ value for each group ($\Delta^{17}\text{O}$ calculated as per samples in this study). Data sources: terrestrial and lunar samples, this study and Starkey *et al.* (19); aubrites, Barrat *et al.* (20); other groups, Greenwood *et al.* (42).

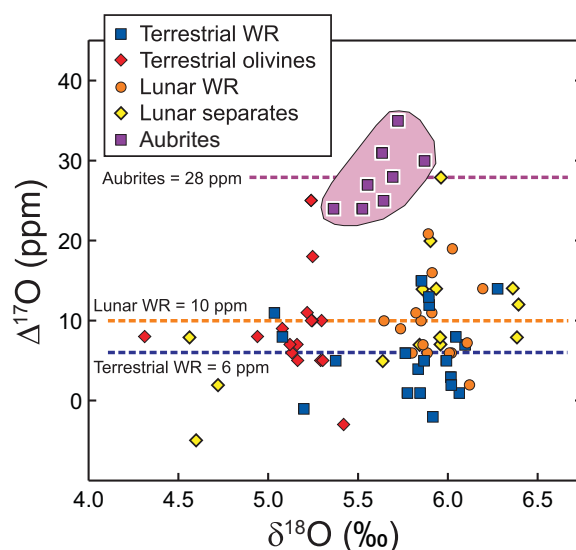


Fig. 2. Oxygen isotopic composition of terrestrial and lunar samples and aubrites. Aubrites are the meteorites with the closest oxygen isotope composition to terrestrial and lunar rocks and, until the study of Barrat *et al.* (20), were thought to be indistinguishable from them. TWR, terrestrial whole rock analyses; LWR, lunar whole rock analyses.

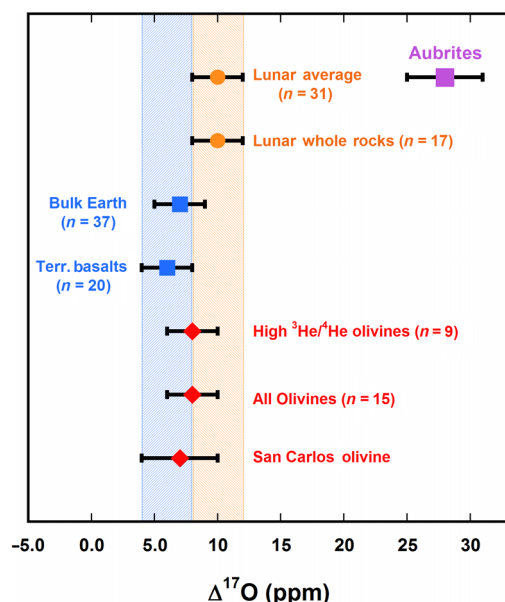


Fig. 3. Average $\Delta^{17}\text{O}$ values of lunar and terrestrial samples measured in this study. Aubrites are also shown (20). Blue ruled box ± 2 SEM variation for terrestrial basalts ($n = 20$); brown ruled box ± 2 SEM variation for lunar whole rocks ($n = 17$). n = number of samples.

interaction might explain why we find a significantly smaller $\Delta^{17}\text{O}$ difference between lunar and terrestrial samples than the 12 ± 3 ppm reported by Herwartz *et al.* (4). However, this is clearly not the case because our olivine samples (table S1), obtained predominantly from sub-aerially erupted lavas (19), have an average $\Delta^{17}\text{O}$ composition that is 3 ppm higher than the terrestrial basalts, which is opposite to what would be predicted if basalts had incorporated significant amounts of seawater-derived oxygen. With a $\Delta^{17}\text{O}$ of -346 ppm relative to the reference line used in this study, a $\sim 1\%$ addition of atmospheric oxygen would be sufficient to account for the measured offset between lunar whole rocks and terrestrial basalts. However, lunar samples would also be sensitive to post-collection air contamination, and identical procedures were used for both sets of specimens. Our pre-reaction procedures should have efficiently removed any adsorbed atmospheric component (see Materials and Methods). It has recently been suggested that $\Delta^{17}\text{O}$ values might be influenced by differences in crystal structure between phases such as olivine, quartz, and feldspar (22, 23). If correct, this would pose significant difficulties for using pure mineral phases, such as San Carlos olivine, as a proxy for the bulk Earth (4, 5). However, in our study, the maximum $\Delta^{17}\text{O}$ Earth-Moon difference is found between terrestrial and lunar basalts, which are multicomponent samples with almost identical $\delta^{18}\text{O}$ values and so provide a sound basis for direct comparison of $\Delta^{17}\text{O}$ values.

We therefore conclude that the 3 to 4 ppm $\Delta^{17}\text{O}$ difference between terrestrial and lunar samples observed in our data, while significantly lower than the 12 ± 3 ppm (SEM) value obtained in a previous study (4), is nonetheless real. We now consider the implications of this slight $\Delta^{17}\text{O}$ difference between lunar and terrestrial samples for the origin and evolution of the Earth-Moon system.

DISCUSSION

Testing an aubritic composition for Theia

There are strong geochemical and isotopic arguments that, throughout its accretion history, Earth formed from material with a high enstatite

chondrite-like component (E-type) and that the final 40% of accretion, including the Moon-forming impactor, was composed almost exclusively of E-type material (17). This is further supported by evidence from the FeO composition, and Nb/Ta and Hf/W ratios, of Earth and the Moon, which favor a reduced (FeO $\sim 0.3\%$) Mercury-like impactor (24). However, the actual enstatite chondrites are poor candidate materials for the Moon-forming impactor, having low Mg/Si ratios and being relatively enriched in volatile elements. They may have formed from the same isotopic reservoir as Earth, but subsequently diverged in their chemical composition from Earth's building blocks (25). In the canonical model (1), the impactor was taken to be Mars-sized and so would have been a fully differentiated body and hence homogeneous with respect to oxygen isotopes. Consequently, when looking for a proxy for this impactor, commonly referred to as Theia, it makes geochemical sense to use an achondrite, which, as a result of high degrees of melting on its parent body, has a homogeneous oxygen isotopic composition (20).

The aubrites provide the closest match to the hypothesized reduced impactor (24), being virtually FeO-free and having an isotopic composition that is closely similar to both Earth and enstatite chondrites (Fig. 1) (20, 26). High-precision oxygen isotope data for aubrites ($n = 8$) (Figs. 1 and 2) show that their oxygen isotopic composition [$\Delta^{17}\text{O} = 28 \pm 3$ ppm (2 SEM)] (table S1) is close to, but fully resolvable from that of Earth and the Moon (Fig. 2). Using the canonical giant impact model (1) (10.6% impactor and 89.4% proto-Earth in the final Earth) and taking the isotopic composition of the impactor to be that of the aubrites, we have calculated the relative proportions of impactor and target material that are required in Earth and the Moon to account for the oxygen isotopic differences observed in our data (model S1). The ~ 4 ppm Earth-Moon difference observed between terrestrial basalts and lunar rocks can be reproduced by a lunar impactor component of 25 to 28% of the Moon's mass, compared to the terrestrial impactor component of 10.4% (Fig. 4). The required impactor contribution is significantly lower than the 70% predicted by the canonical model (1) and also less than other low-velocity scenarios (Fig. 4) (27). The SE of our observed 4 ppm Earth-Moon difference is ± 3 ppm (2 SE), which would indicate that the range of permissible impactor contributions to the Moon is between 13 and 39% (Fig. 4). It has been shown that the proto-Earth and the impactor were isotopically similar before collision (28). Our analysis indicates that aubrites are distinct enough to exclude them as an impactor candidate if no Earth-Moon homogenization took place. EH (high-Fe) and EL (low-Fe) enstatite chondrites are also possible candidates, but these meteorites have heterogeneous oxygen isotopic compositions, resulting in group average $\Delta^{17}\text{O}$ values that are highly uncertain (Fig. 1). The EH and EL impactor scenarios therefore cannot be tested with currently available oxygen isotope data. Assuming that aubrites represent faithful proxies for the oxygen isotopic composition of all enstatite-type impactors, we conclude that the present $\Delta^{17}\text{O}$ similarity between Earth and the Moon is unlikely to be due to the impactor and the proto-Earth having nearly identical isotopic compositions. If correct, this implies that the isotopic compositions of Earth and the Moon were homogenized as part of the equilibration processes associated with the giant impact event itself.

Although high-energy collisional models (2, 3) predict a lower compositional difference between Earth and the Moon than the canonical model (1), they do not envisage complete isotopic homogenization. Thus, the average of all the Δ^{proj} values in table 3 of the work by Čuk and Stewart (2) (Δ^{proj} = difference in projectile mass fraction between the silicate portions of the planet and disc) is 8.8%, which, with the use of

a terrestrial $\Delta^{17}\text{O}$ value of 6 ppm and an impactor value of 28 ppm (aubritic), equates to a Moon-Earth difference of 2 ppm, that is, about half that represented by our lunar and terrestrial whole rock analyses. A similar value is obtained for those runs that are deemed by Čuk and Stewart (2) to be successful Moon-forming scenarios. In the simulations of Canup (3), the disc can contain more or less impactor material than the final planet. For those runs in which the disc contains more impactor material, the overall average difference between the disc and the final planet was approximately 8%, similar to that predicted by the simulations of Čuk and Stewart (2) and indicating a Moon-Earth difference of about 1.8 ppm. It is worth noting that some of the runs of Canup (3), such as run 17, essentially envisage complete mixing between the target and the impactor. The synestia scenario for the formation of the Earth-Moon system, involving substantial and possibly multiple vaporization events (13, 14), is likely to result in essentially complete isotopic homogenization of the entire system, with the possible exception of some very deep primordial mantle reservoirs (15).

As discussed above, the 3 to 4 ppm $\Delta^{17}\text{O}$ difference between the terrestrial and lunar rocks analyzed in this study is not consistent with an aubritic impactor, unless some form of post-impact equilibration also took place. In the absence of such an equilibration event, the impactor would have had to have been much closer to the proto-Earth in its oxygen isotopic composition than the aubrites. This is not impossible, but we would argue that it is unlikely. Our results are consistent with high-energy impact simulations (2, 3) and potentially consistent with a limited differential impactor component in the Moon compared to

Earth. However, if total oxygen isotopic equilibration took place in the aftermath of the giant impact, as appears to be implied by the synestia model (13, 14), then the 3 to 4 ppm Earth-Moon $\Delta^{17}\text{O}$ difference requires a post-impact explanation. We now explore this possibility further here.

Differential post-impact additions to Earth and the Moon

Highly siderophile element data indicate that following the giant impact, both Earth and the Moon received an input of chondritic material, generally referred to as the late veneer (29). However, the amounts accreted by Earth and the Moon were very different: ~0.5 weight % (wt %) of the terrestrial mass and ~0.02 wt % of the lunar mass (29). This may reflect the involvement of a limited number of larger asteroids, which differentially impacted Earth (30). From an oxygen isotope perspective, the relatively small late veneer contribution to the Moon can be neglected. We assume that the average lunar $\Delta^{17}\text{O}$ value is representative of the post-giant impact, pre-late veneer, terrestrial composition ($\Delta^{17}\text{O} = 10 \pm 2$ ppm) and show the effects of adding various chondritic components to it in Fig. 5 and fig. S4. The shaded vertical band in Fig. 5 is the error (± 2 SEM) on the average terrestrial basalt $\Delta^{17}\text{O}$ value. Addition

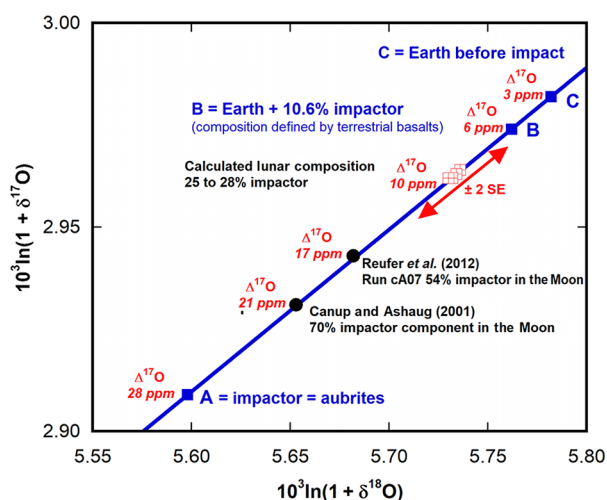


Fig. 4. Diagram showing calculated oxygen isotopic composition of lunar rocks assuming an impact scenario defined by the canonical model (1). The oxygen isotope composition of the impactor is assumed to be that of the aubrites (table S1) and the composition of Earth following the giant impact is given by the terrestrial basalt samples analyzed in this study. These calculations indicate that the observed 4 ppm difference between terrestrial basalts and lunar rocks would require the Moon to be composed of between 25 and 28% impactor-derived material. This is significantly less than predicted by low-energy impact models in the absence of post-impact equilibration (1, 27). The SE of the 4 ppm difference is ± 3 ppm (2 SE), which would indicate that the range of permissible impactor contributions to the Moon is between 13 and 39%. Note that apart from the aubrite (impactor) and terrestrial basalt data (Earth proxy), all other points on the diagram are calculated. These calculations can only predict $\Delta^{17}\text{O}$ values (shown in italics) and not the measured $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values, which, for natural samples, will be influenced by a variety of mass-dependent fractionation processes.

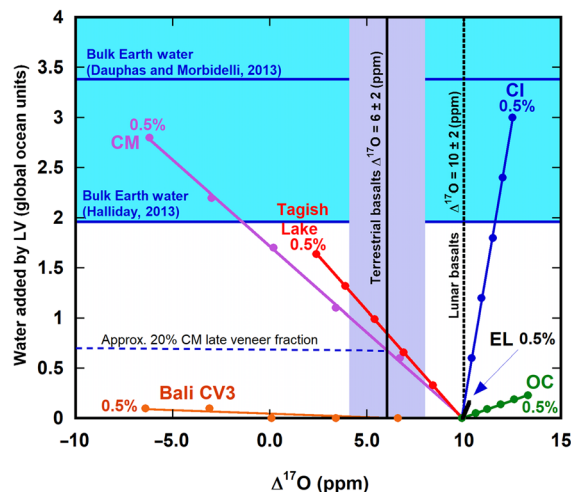


Fig. 5. Diagram showing how the addition of various chondritic components as part of the late veneer would alter the average $\Delta^{17}\text{O}$ value of pristine terrestrial mantle. The $\Delta^{17}\text{O}$ composition of pristine terrestrial material just after the giant impact is taken to be equivalent to that of present-day lunar basalts. A late-stage addition of any single chondritic component in an amount equivalent to the late veneer mass would result in a $\Delta^{17}\text{O}$ isotopic shift greater than that defined by the 2 SEM error envelope of the terrestrial basalts (purple vertical band). An appropriate mix of chondritic components such as CI and CM would not violate the constraints imposed by our data. However, such a high percentage of chondritic material would violate Ru isotope constraints (31). A late veneer addition of 0.5% terrestrial mass of enstatite chondrite material (EL) (short black line) would add little water and result in only a very slight deviation to the $\Delta^{17}\text{O}$ value of the lunar basalts. A CM late veneer fraction of approximately 20% (horizontal blue dashed line) can account for the 3 to 4 ppm $\Delta^{17}\text{O}$ shift measured in the terrestrial basalts, while maximizing the amount of water delivered to Earth and minimizing the CC component within the late veneer, as required by Ru isotope systematics (31). An input of about 20% CV3 (Vigarano-type carbonaceous chondrite) would also satisfy the $\Delta^{17}\text{O}$ constraints, but reduce the amount of water delivered by the late veneer. On the basis of the lowest estimates of Earth's water content (33), the late veneer, at best, could only have supplied about one-third of our planet's water. Higher global water estimates (32) would decrease this to about 5% (see the Supplementary Materials). Dots on the lines refer to 0.1% of terrestrial mass. OC, ordinary chondrite; LV, late veneer.

of CI (Ivuna-type carbonaceous chondrites) or ordinary chondrite-like materials to lunar basalts would increase their $\Delta^{17}\text{O}$ value away from present-day terrestrial compositions, suggesting that these materials did not form a predominant component of the late veneer. This conclusion is supported by the results of Ru isotope analysis (31). Compared to terrestrial samples, which have an average $\epsilon^{100}\text{Ru}$ value of +0.05, CIs have a value of −1.03 and ordinary chondrites have an average value of −0.29 (31). In comparison, enstatite chondrites, with an average value of −0.08, are the closest to terrestrial materials and hence likely to be the main component of the late veneer (12, 31). However, enstatite chondrites have average $\Delta^{17}\text{O}$ compositions that are heavier than those of lunar basalts [EL group, 48 ± 14 (2 SEM) ppm heavier; EH group, 23 ± 18 (2 SEM) ppm heavier] (4), and hence, a late veneer of exclusively enstatite chondrite would shift terrestrial materials to higher $\Delta^{17}\text{O}$ values, rather than the lower values that are observed (Fig. 5 and fig. S4). Therefore, the late veneer likely contained a chondritic component with a significantly negative $\Delta^{17}\text{O}$ composition, with the most obvious candidates being carbonaceous chondrites (CCs), excluding CIs (Fig. 5 and fig. S4).

In terms of hydrated CCs, both CMs (Mighei-type carbonaceous chondrites) and the ungrouped CC Tagish Lake have the potential to explain the $\Delta^{17}\text{O}$ offset between terrestrial basalts and lunar whole rocks and could also have provided a significant proportion of Earth's water (Fig. 5). At present, there is little consensus concerning the amount of water present in Earth, with estimates varying between about 2 and 12 global ocean units (32–34) (global ocean unit = total mass of hydrosphere = 1.38×10^{21} kg) (35). On the basis of the lowest of these estimates (33), a late veneer composed exclusively of any of the hydrated CC end members (CI, CM, and Tagish Lake) could have furnished all, or most, of Earth's water. However, such a high CC content would violate the oxygen isotope constraints imposed by our data, as well as those from Ru isotopes (31). CM chondrites could provide the 4 ppm $\Delta^{17}\text{O}$ shift required by our terrestrial basalt data, while forming a relatively low fraction of the late veneer, as required by the Ru isotopes (31). A late veneer composition consisting of approximately 20% CM and 80% enstatite chondrite best fits the $\Delta^{17}\text{O}$ and Ru isotope constraints (Fig. 5). However, this would provide only about 0.7 of a global ocean unit and, based on the most conservative estimates (33), represents only about 30% of Earth's water budget. If higher global water estimates are realistic (32), then the late veneer, at best, delivered only about 5% of our planet's water (see Materials and Methods) (fig. S4). CV3 chondrites, which are essentially dry, would equally fulfill the $\Delta^{17}\text{O}$ constraints set by our study, but provide even less water (Fig. 5 and fig. S4).

A late veneer explanation for the 3 to 4 ppm $\Delta^{17}\text{O}$ Earth-Moon difference implies that a large fraction of Earth's water was delivered earlier than the giant impact event. Terrestrial hydration would have been synchronous with the main phase of Earth's accretion and not the result of a late-stage delivery of water from the outer solar system (36). Fortuitously for the evolution of life on our planet, despite the high energy of the Moon-forming event, Earth retained enough of its primordial water to remain a habitable environment. These findings are consistent with modeling studies, which indicate that Earth would have had an ocean before the era of giant impacts and that this ocean was retained despite the high energy of this terminal accretion phase (37). Retention of early accreted water on Earth may have more general implications for the habitability of exoplanetary systems, which commonly experience similar early-stage, high-energy collisional processing (38).

MATERIALS AND METHODS

Materials

Terrestrial samples were selected to be representative of mantle melt compositions and to have experienced minimal interaction with the continental crust, atmosphere, and hydrosphere. A summary of these samples is given in table S3. Oceanic samples were selected to include ridge segments from all the major oceans (Indian, Pacific, Atlantic, and Pacific-Antarctic). They are all pure glasses and show no evidence of seawater interaction. In addition to the diversity of the areas sampled, a wide range of compositions were selected, ranging from normal mid-ocean ridge basalt (N-MORB) to enriched MORB (E-MORB). The oceanic suite also includes one relatively evolved sample, HYAMS/DR3-10, which is a benmoreite glass. Ocean island basalts include the following: (i) BHVO2, a U.S. Geological Survey (USGS) rock standard that was produced by sampling 1911 pahoehoe lava from Hawaii; (ii) BIR1, a USGS rock standard produced by sampling interglacial basalt flow near Reykjavik, Iceland; (iii) C13, very fresh evolved lava—trachybasalt; and (iv) PIF-1 and PIF-2, samples from very fresh, vesiculated, picritic lava erupted in 2006 and collected approximately 1 month later.

The terrestrial olivine mineral separate data discussed in this paper have been presented previously (19). However, as discussed below, the data have been recalibrated to VSMOW using more recent isotopic values for the Open University's laboratory standard gas (O_2 -8). Details of collection locations, composition, and mineralogy of these samples have been presented previously (19).

Lunar whole rock and mineral separates analyzed in this study include samples from all the Apollo landings: Apollo 11 (10020 and 10044), Apollo 12 (12016 and 12040), Apollo 14 (14053), Apollo 15 (15016, 15059, 15386, and 15555), Apollo 16 (62237 and 67435), and Apollo 17 (70017, 70035, 71055, 72155, and 78235). All of the major lunar rock suites are also covered by the samples analyzed in this study: high- and low-Ti Mare basalts, olivine normative basalts, KREEP basalts, and highland suite lithologies.

Lunar mineral separates (olivine, orthopyroxene, clinopyroxene, plagioclase, and ilmenite) from one Apollo 15 sample (15016) and three Apollo 17 samples (70017, 71055, and 72155) prepared at the University of Chicago (39, 40) were reanalyzed as part of this study (table S1).

Laser fluorination analysis

Oxygen isotopic analysis was undertaken at the Open University using an infrared laser fluorination system (41). ~2 mg aliquots of samples and standards were loaded into a Ni sample block containing 22 drilled wells. The sample block was then placed in a two-part chamber, made vacuum-tight using a compression seal with a copper gasket and a quick-release KFX clamp (41). A 3 mm-thick BaF_2 window at the top of the chamber allowed simultaneous viewing and laser heating of samples. After sample loading, the cell was heated under vacuum for a minimum of 24 hours and to a temperature of at least 70°C to remove any adsorbed atmospheric moisture. Before fluorination, the system blank was systematically reduced by flushing the chamber with aliquots of BrF_5 , such that the final blank was less than 60 nmol O_2 . As a consequence of these procedures, potential problems associated with retained adsorbed moisture were minimized (5). Sample heating in the presence of BrF_5 was carried out using an integrated 50 W infrared CO_2 laser (10.6 μm) and video system mounted on an X-Y-Z gantry supplied by Photon Machines Inc. (42). After fluorination, the released O_2 was purified by passing it through two cryogenic (liquid nitrogen) traps and over a bed of heated KBr. The isotopic composition of the purified oxygen was analyzed using a Thermo Fisher MAT 253 dual-inlet

mass spectrometer (mass resolving power, 200). Interference at m/z (mass/charge ratio) = 33 by NF_2^+ was monitored by performing scans for NF_2^+ on the sample gas before analyzing each sample; this was below interference levels during all sample analyses reported here. Our current system precision based on repeat analyses ($n = 39$) of our obsidian internal standard is $\pm 0.052\text{‰}$ for $\delta^{17}\text{O}$, $\pm 0.094\text{‰}$ for $\delta^{18}\text{O}$, and $\pm 0.017\text{‰}$ for $\Delta^{17}\text{O}$ (2σ) (19).

Calibration of samples using the VSMOW scale

Oxygen isotope measurements of rocks and minerals are generally reported relative to VSMOW. However, direct calibration of the “laboratory standard” O_2 gas by comparison with O_2 prepared by direct fluorination of VSMOW is technically challenging. Therefore, most laboratories that measure oxygen triple-isotope ratios in rocks and minerals calibrate their own laboratory standard O_2 against oxygen generated from fluorination of one or more widely used silicate standards, such as NBS-28, UWG-2 garnet, or San Carlos olivine. However, this procedure is problematic and, for high precision analysis, the laboratory standard O_2 should be calibrated against VSMOW directly (43). The Open University laboratory standard gas (referred to as O_2 -7) used in earlier studies (44) subsequently became exhausted and was replaced by O_2 -8, which was used in this study. Pending a full VSMOW calibration, O_2 -8 was initially calibrated against a limited range of secondary standards, as is normal practice in many laboratories. A more direct calibration of O_2 -8 relative to VSMOW was subsequently undertaken at the Hebrew University of Jerusalem. All $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data obtained during this study were then recalculated to the VSMOW scale based on the independent measurements of our O_2 -8 laboratory standard gas. Data for terrestrial olivine samples (19) and aubrites (20) analyzed at the Open University, using the same (O_2 -8) laboratory standard gas, were recalibrated in the same way.

Choice of assigned reference fractionation line (slope λ and ordinate axis offset γ)

With regard to an appropriate value of λ , some authors have assigned a value based on the actual fractionation line given by a collection of terrestrial samples (7, 18, 45), whereas others have assigned the high temperature limit value for oxygen isotope exchange under equilibrium conditions, 0.5305 (43, 46). There is, as yet, no consensus on a reference line for defining $\Delta^{17}\text{O}$ values of silicate rocks and minerals. This can lead to misleading comparisons, if care is not taken to ensure that all $\Delta^{17}\text{O}$ values are defined consistently. An additional complication is that it has recently been shown that terrestrial rocks and minerals form fractionation arrays that are slightly offset (by approximately -30 to -70 ppm) from the VSMOW reference (18, 47). Accordingly, and based on the fractionation line obtained from measurements at the Open University laboratory for a set of eclogitic garnets supplied by D. Rumble of the Carnegie Institution of Washington, DC, $\Delta^{17}\text{O}$ values reported in this study, including those of terrestrial olivines (19) and aubrites (20) (table S1), are reported using a λ value of 0.5262 and a VSMOW offset (γ) of -64 ppm. Our reason for using this particular reference line is that it is both well constrained and reproducible. We reanalyzed those garnets at the start of this project and obtained an identical slope value to our previously published results (48). These new analyses of the eclogitic garnets are given in table S4 and plotted in fig. S5.

Slope and intercept values for lunar and terrestrial samples

The $10^3 \ln(1 + \delta^{17}\text{O})$ versus $10^3 \ln(1 + \delta^{18}\text{O})$ values of all the terrestrial and lunar samples discussed in this paper (table S1) are plotted in fig. S1.

The best-fit line had a slope of 0.5285 ± 0.0016 and a y -axis intercept of -0.068 ± 0.009 . Because of the limited range of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values, the error on this line was significantly greater than that for the eclogitic garnets (table S4 and fig. S5). Note that, at the level of precision in this study, the concept of a single TFL is not valid (44). All lunar oxygen isotope data measured in this study, filtered such that samples with $\Delta^{17}\text{O}$ reproducibility of greater than 6 ppm SEM were excluded, are plotted in fig. S2. The best-fit line through the data had a slope of 0.5301 ± 0.0024 and a y -axis intercept of -0.077 ± 0.014 . While the slope through the data was close to the theoretical upper limit of 0.5305 (18, 43), it should be noted that the error associated with this slope was large due to the limited range in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values. All of the oxygen isotope data from terrestrial basalt samples measured in this study, filtered to exclude samples with $\Delta^{17}\text{O}$ reproducibility of greater than 6 ppm SEM, are plotted in fig. S3. The best-fit line through the data had a slope of 0.5270 ± 0.0037 and a y -axis intercept of -0.062 ± 0.021 . The slope through the terrestrial basalt data was somewhat lower than that for the lunar samples (fig. S2), but in both cases, the limited range in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values meant that there was a significant level of uncertainty on the slope and y -axis intercept values for both.

Statistical analysis

The mean $\Delta^{17}\text{O}$ values of the lunar whole rocks and terrestrial basalts measured in this study were very similar, 10 ± 10 ppm (2 SD) and 6 ± 10 ppm (2 SD), respectively (SD) (table S1). Previous claims that lunar and terrestrial samples had essentially identical oxygen isotopic compositions were also based on the close similarity of their respective mean $\Delta^{17}\text{O}$ values and overlapping distributions about those means, as measured using SD (6–8). However, if no systematic bias is present, a more appropriate test to compare the two populations is to use the $\text{SEM} = \text{SD}/\sqrt{n}$ (4). On this basis, the full suite of lunar whole rocks and mineral separates analyzed in this study ($n = 31$) had a mean $\Delta^{17}\text{O}$ composition of 10 ± 2 ppm (2 SEM) and the terrestrial samples ($n = 20$) had a mean $\Delta^{17}\text{O}$ composition of 6 ± 2 ppm (2 SEM) (table S1). One study (4) detected a 12 ± 3 ppm oxygen isotope difference between Earth and the Moon. However, this was based on only 3 lunar basalts and 8 terrestrial samples (11 if mineral separates are counted as individual samples). These findings were challenged by a subsequent study, which concluded that the Moon and Earth were isotopically indistinguishable at the ± 5 ppm (2 SEM) level (5). However, this study was also based on a relatively small suite, comprising 8 lunar samples and 4 terrestrial samples (6 if mineral separates are counted as individual samples). The present study was based on 16 distinct lunar samples (32 if mineral separates were counted as individual samples) and 21 distinct terrestrial samples. The terrestrial data were augmented by 13 distinct olivine fractions (19) analyzed at the Open University under identical conditions to the data in the present study.

In view of the small difference between the mean $\Delta^{17}\text{O}$ composition of the terrestrial and lunar suites, one potential problem in using analyses collected over extended time periods is the possibility of some form of analytical drift, perhaps resulting from a change in the isotopic composition of the reference gas. To examine this possibility, we have compiled all the obsidian standards data obtained throughout the course of this study. The analyses from our olivine study (19) were made during 2012 to 2014, whereas the terrestrial and lunar samples data were obtained during 2014 to 2016. Longer-term systematic drift between the lunar whole rocks and mineral separates and terrestrial samples was unlikely because these were analyzed sequentially. There was a slight

overlap in time between the two studies, of about 3 months. For the compilation of obsidian standards data (data are available in a spreadsheet file), we have eliminated the first obsidian run in each tray because this is sometimes affected by a comparatively high blank contribution, as reflected in a systematically higher $\delta^{18}\text{O}$ value than obsidian samples run later in the same tray. Figure S6 shows a histogram of obsidian standards data collected during 2012 to 2014 compared with obsidian data collected during 2014 to 2016. Both sets of data show almost identical distributions, with the exception of a few higher values obtained during 2012 to 2014. The mean values for $\Delta^{17}\text{O}$ in the two periods were essentially identical: 15.7 ± 2.6 ppm (2 SEM) ($n = 91$) for the period 2012 to 2014 and 15.5 ± 2.4 ppm (2 SEM) ($n = 64$) for the period 2014 to 2016. On the basis of these data, it is clear that the Open University system was analytically very stable throughout the period of this study and that it was entirely reasonable to combine the data for terrestrial olivines (19) with the lunar and terrestrial analyses collected as part of the present study.

The large sample suite provided by our study allows for a full statistical analysis of possible differences between the oxygen isotopic compositions of Earth and the Moon. It is likely that the more limited number of samples used in previous studies (4, 5) was the main reason for their seemingly contradictory results. The larger sample set used in this study allowed us to demonstrate that a lunar-terrestrial $\Delta^{17}\text{O}$ difference does exist, in contradiction to the findings of Young *et al.* (5), but is much less pronounced than claimed by Herwartz *et al.* (4). Results of Student *t* tests for unpaired data with equal variance are given in table S2. Details of additional statistical analysis undertaken to test the significance of the difference in mean values between our terrestrial and lunar samples are given in the Supplementary Materials.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/3/eaao5928/DC1>

Supplementary Text

fig. S1. Linearized oxygen isotope plot for all terrestrial and lunar samples analyzed in this study ($n = 68$), including the terrestrial olivines (19).

fig. S2. Linearized oxygen isotope plot for all filtered lunar samples ($n = 24$) analyzed in this study.

fig. S3. Linearized oxygen isotope plot for all filtered terrestrial basalt samples ($n = 18$) analyzed in this study.

fig. S4. Diagram showing how addition of various chondritic components would alter the isotopic and water abundance compositions of the post-giant impact Earth.

fig. S5. Oxygen isotope composition of eclogitic garnets.

fig. S6. Obsidian standards data collected during this study compared to data collected during the earlier terrestrial olivine study (19).

fig. S7. Kernel estimate densities from samples' average values.

fig. S8. Kernel estimate densities from raw data (all replicates run for all samples).

table S1. Full listing of oxygen isotope data.

table S2. Results of Student *t* tests for unpaired data with equal variance.

table S3. Whole rock terrestrial samples.

table S4. Analyses of eclogitic garnet samples.

table S5. Oxygen isotope analyses and water content values used to construct Fig. 5 and fig. S4 (Excel file).

table S6. Late veneer end member calculations used to construct Fig. 5 and fig. S4 [Excel files (x6)].

table S7. Water in Earth: Calculations used to construct Fig. 5 and fig. S4 (Excel file).

model S1. A spreadsheet that calculates the oxygen isotopic composition of the Moon using a mix defined by our analyses of terrestrial basalts and aubrites (20) (Excel file).

model S2. A spreadsheet that calculates the oxygen isotopic composition of the Moon using a mix defined by our analyses of olivines and aubrites (20) (Excel file).

Compilation of all replicate analyses run in this study (Excel file).

Compilation of obsidian standards data 2012–2014 (Excel file).

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Oxygen isotopic evidence for accretion of Earth's water before a high-energy Moon-forming giant impact

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